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MEMORANDUM FOR PRS (In-House Publication)

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15 April 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-082**
Rusty Blanski et al. (PRSM), "Hybrid Inorganic-Organic Performance Fluids Based on Polyhedral Oligomeric Silsesquioxanes (POSS)"

SAMPE Industry Conference
(Long Beach, CA, 12-15 May 2002) **(Deadline: 12 May 2002)** **(Statement A)**

CC of 02-082

rec'd 4/24/02 JR

HYBRID INOI ORGANIC PERFORMANCE FLUIDS BASED ON POLYHEDRAL OLIGOMERIC

CC rec'd from B. Viers 4/24/02 JR

SILSESQUIOXANES (POSS)

Rusty Blanski, Justin Leland,

Brent Viers and Shawn H. Phillips

PRSM

Air Force Research Laboratory

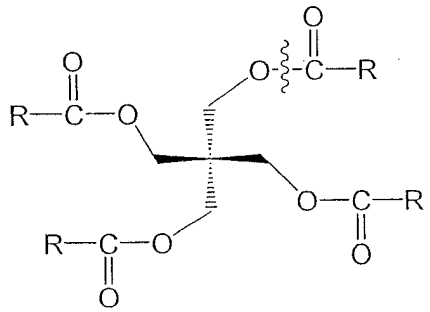
Hybrid Fluids Introduction

Hybrid Performance Fluids are fluids that can operate at elevated temperatures under extreme conditions for a variety of applications such as hydraulic and transmission fluids as well as lubricants. One area the AF is interested in is high temperature lubricants.

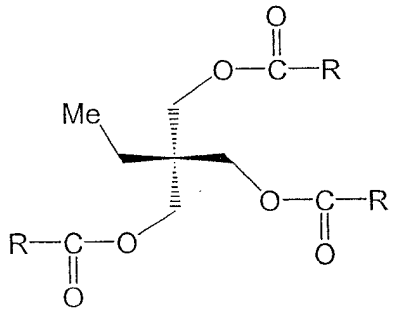
- Goals - Develop a lubricant that can withstand high temperatures (>> 200 °C) and flows at -40 °C (20K centistoke) (High temp gas turbine engines: jets)
- Higher temperature lubes means higher operating temperature >>more power: increase in thrust:weight ratio
- Objective - Synthesize an oil with an operating range of

  - 40 °C to >> 200 °C

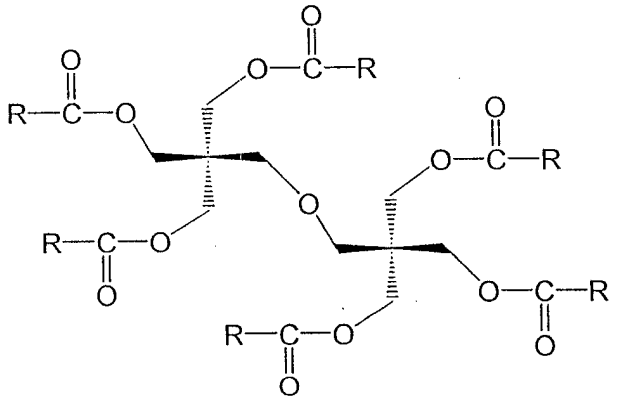
Present AF Lubricants Technology



Pentaerithritol Ester



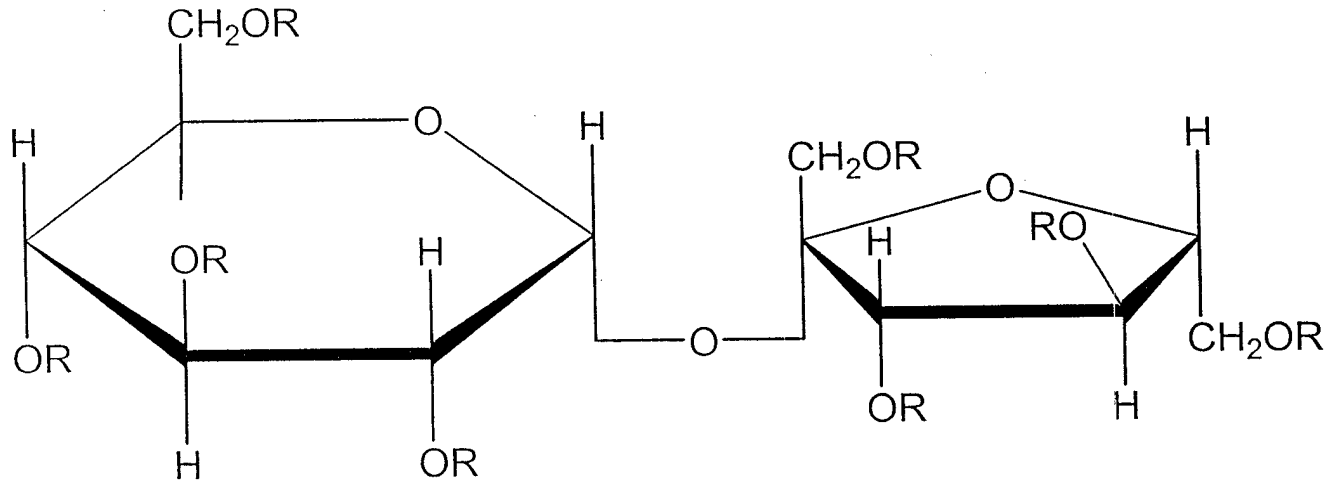
Trimethyloproane Ester



Pentaerithritol Dimer Ester

- **The above polyol ester compounds are the main components of some AF turbine lubricants**
- **Operating range of –40 °C to 200 °C**
- **In house calculations show that ester C-O linkage breaks at 200 °C**

Olestra as a Lubricant?



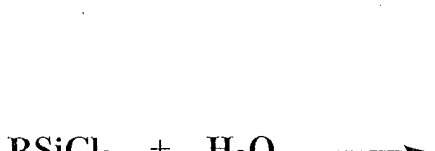
Olestra R = $C_5H_{13}C{=}O$, $C_6H_{15}C{=}O$, $C_7H_{13}C{=}O$ (Merck Index)
Our Sample: sludge w/unsaturated fatty esters present (NMR)
Average chain length: 15.7

Isolated from a Bag of Lays WOW® Brand Potatoe Chips by ether extraction and hydrogenation
Solid at room temperature (Avg chain length: 15.7)
Good Mass loss at 200 °C (only 26% over 9 hours)
Remainder a carmelized sludge

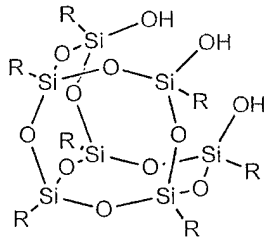
What About a Hybrid Fluid?

- Hybrid organic/inorganic materials have in the past shown superior temperature stability
- One such material that has potential is POSS

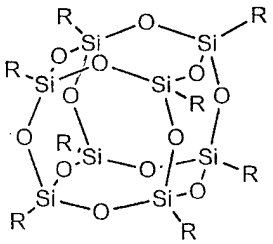
POSS = Polyhedral Oligomeric Silsesquioxane: General Synthesis



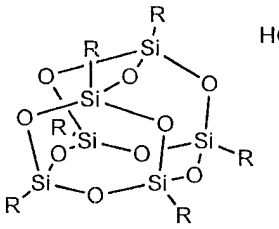
R =Cyclohexyl
Cyclopentyl
Cycloheptyl
Vinyl
Methyl



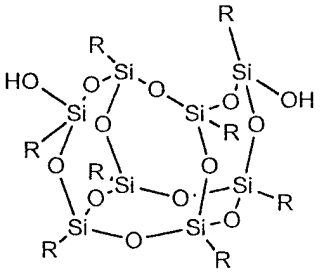
R = Cyclohexyl
Cyclopentyl
Cycloheptyl



R =Cyclohexyl
Cyclopentyl
Vinyl
Methyl



R = Cyclohexyl



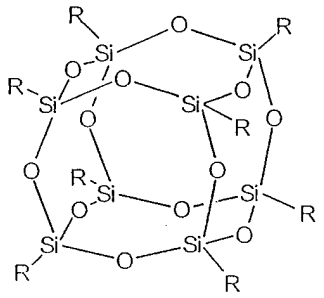
R = Cyclohexyl

R=Cyclohexyl: Brown and Vogt 1965
Feher, Newman, Walzer 1989
Lichtenhan (AFRL, mid '90's) Optimized Purification
Cyclopentyl: Feher, Budzichowski, Weller, Blanski, Ziller 1990
Lichtenhan (AFRL, 1993) Optimization

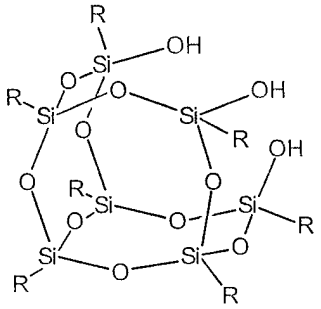
All of these materials are colorless solids at ambient temp

New POSS Synthesis increasesDiversity

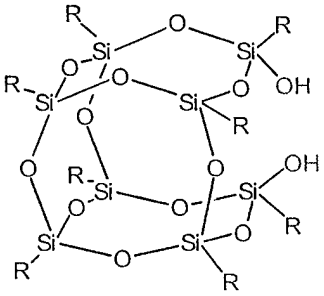
Hybrid Plastics



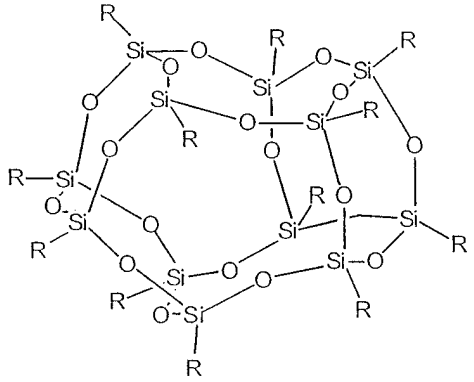
R = Methyl
Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl
Phenyl
Phenethyl
Octadecene



R = Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl
Ethyl
Phenyl



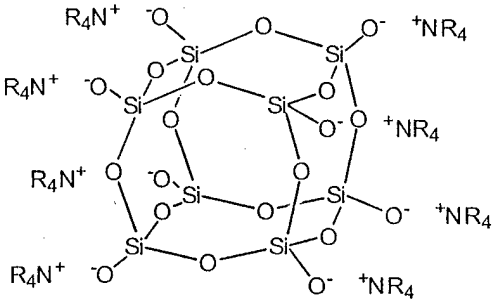
R = Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl



R = Phenyl
Trifluoromethylpropyl

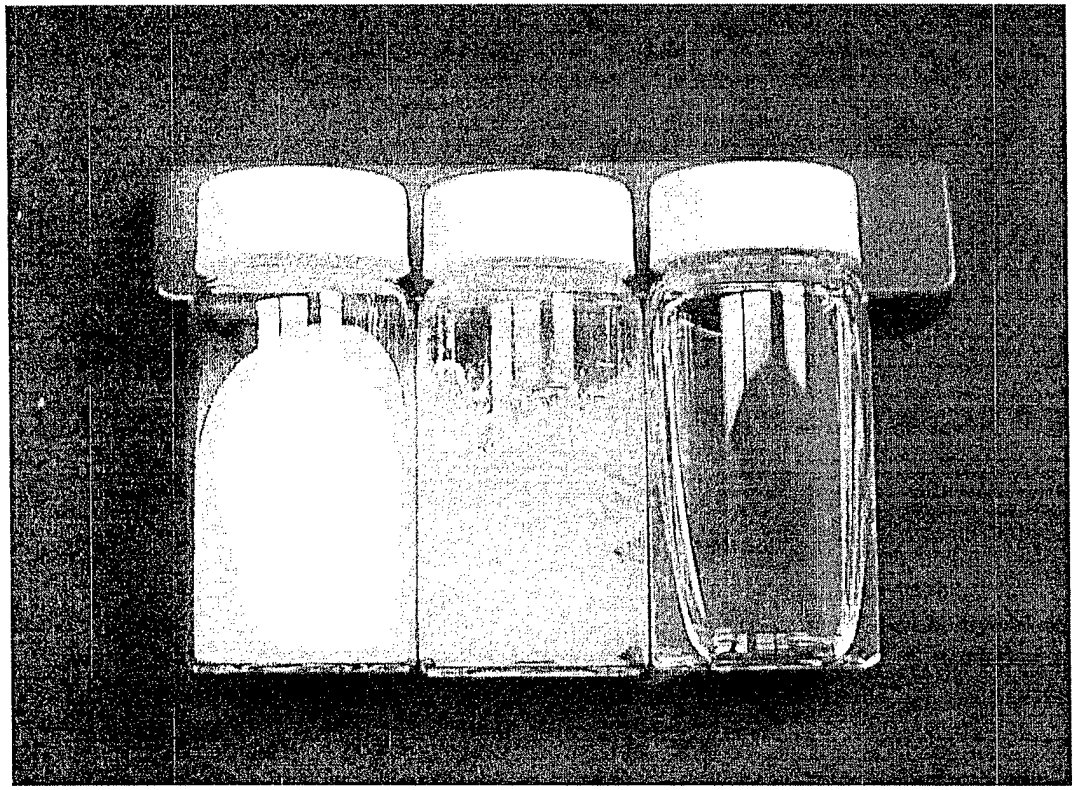
Polydisperse Cages
(T_8, T_{10}, T_{12})

R = Vinyl
Methacrylprpopyl
Phenethyl



R = Methyl

Tech Challenges for Hybrid Oils



Solids Waxes Oils

melts 24°C to 400°C+

viscosity 40cSt. to 400cSt

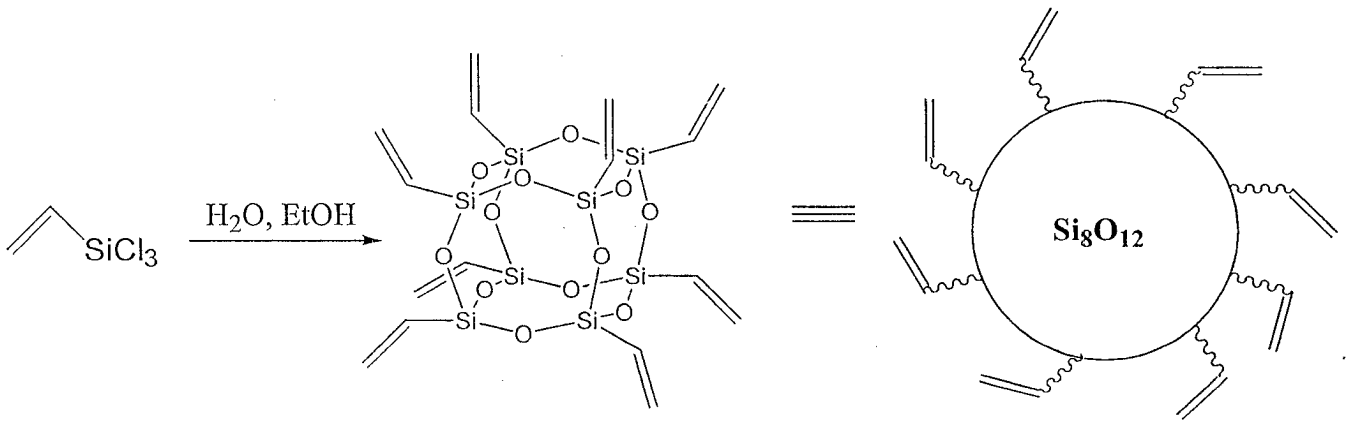
Known POSS molecules decompose to sand

Most POSS molecules are solids at room temperature with only one exception (which does not meet the low temperature pumpability requirements)

Hybrid Plastics

POSS Lubricants Project

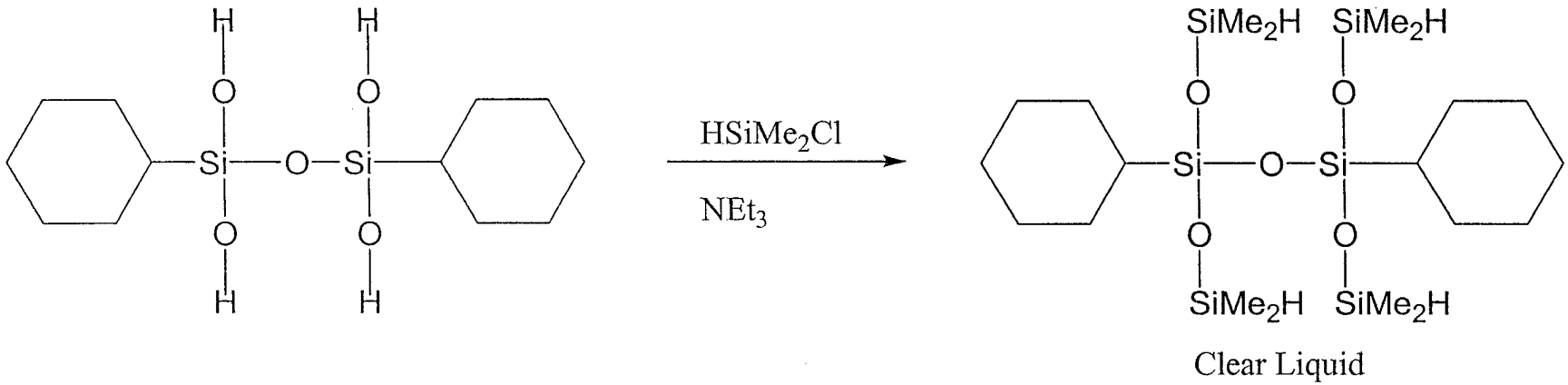
Synthesis of $Vinyl_8T_8$ POSS Base Stock



before: 20% yield (AFRL)
now: 40% yield (Hybrid Plastics)

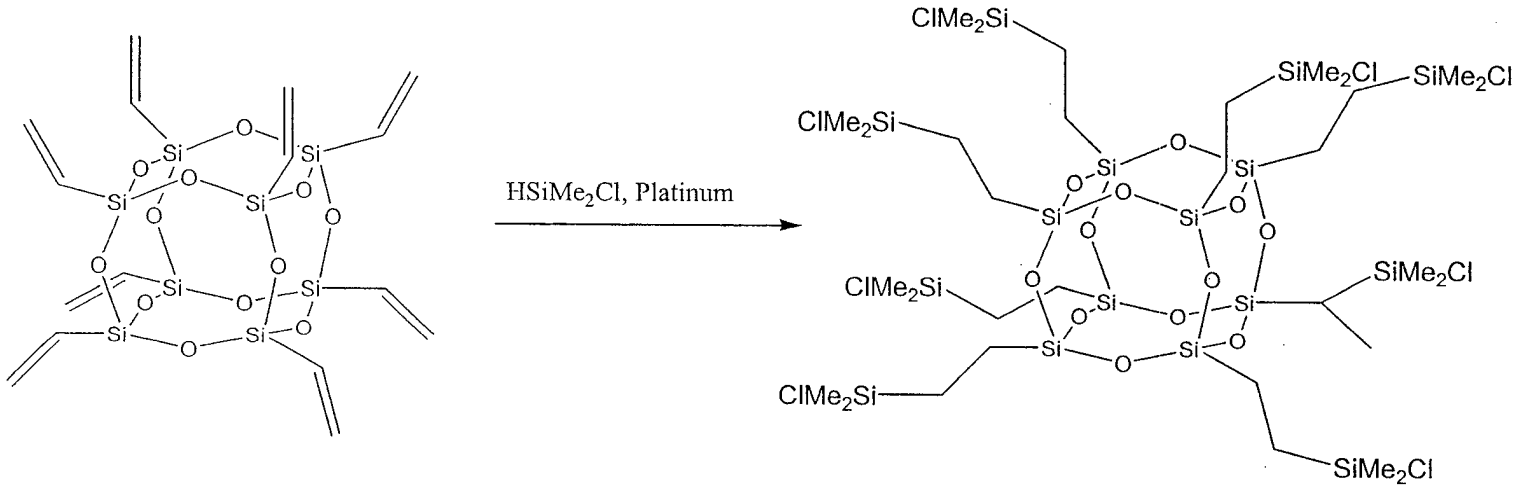
-Least expensive octafunctionalized POSS to date
-Common starting point for octafunctional materials
-CRADA with Hybrid Plastics further reduces cost

POSS Cy_2T_2 Tetrahydride Synthesis

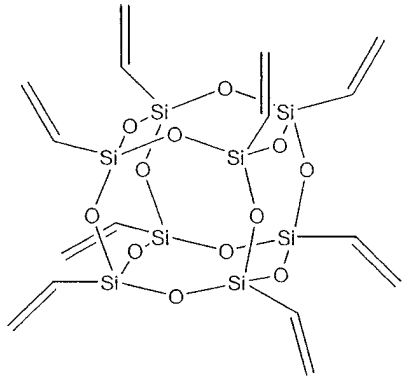


Clear Liquid

POSS Synthesis
Hydrosilation



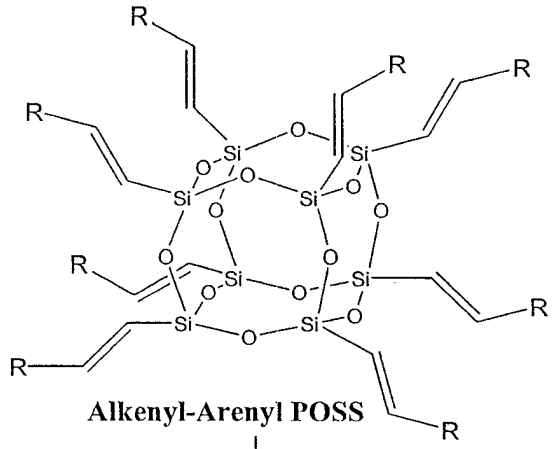
POSS Synthesis
Cross Metathesis/Hydrogenation



$Cl_2Ru(=CHPh)(PCy_3)_2$

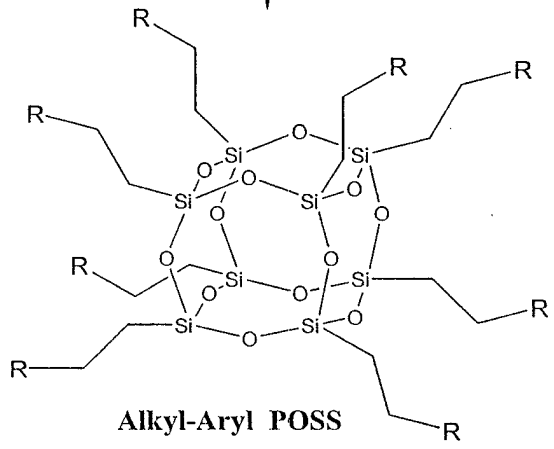
Toluene/arene/alkene

$-C_2H_4$



Alkenyl-Arenyl POSS

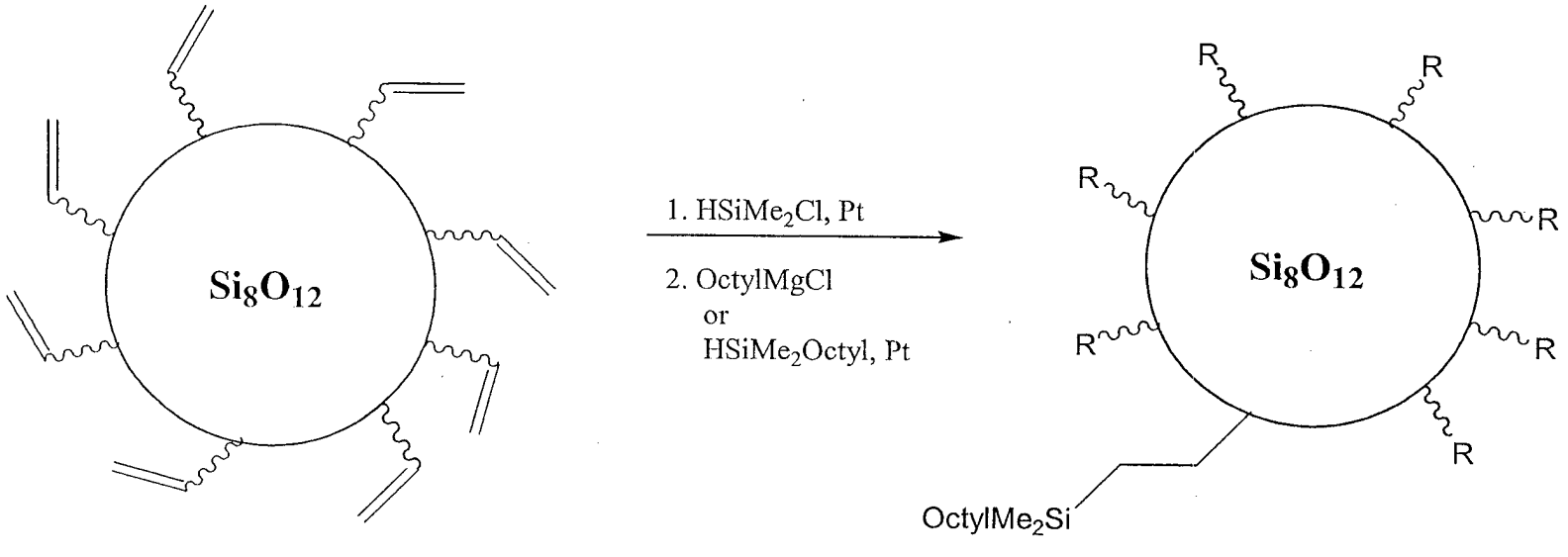
H_2 Pd/C



Alkyl-Aryl POSS

Very useful reaction:
Can potentially have
8 different R groups
on the Cage!

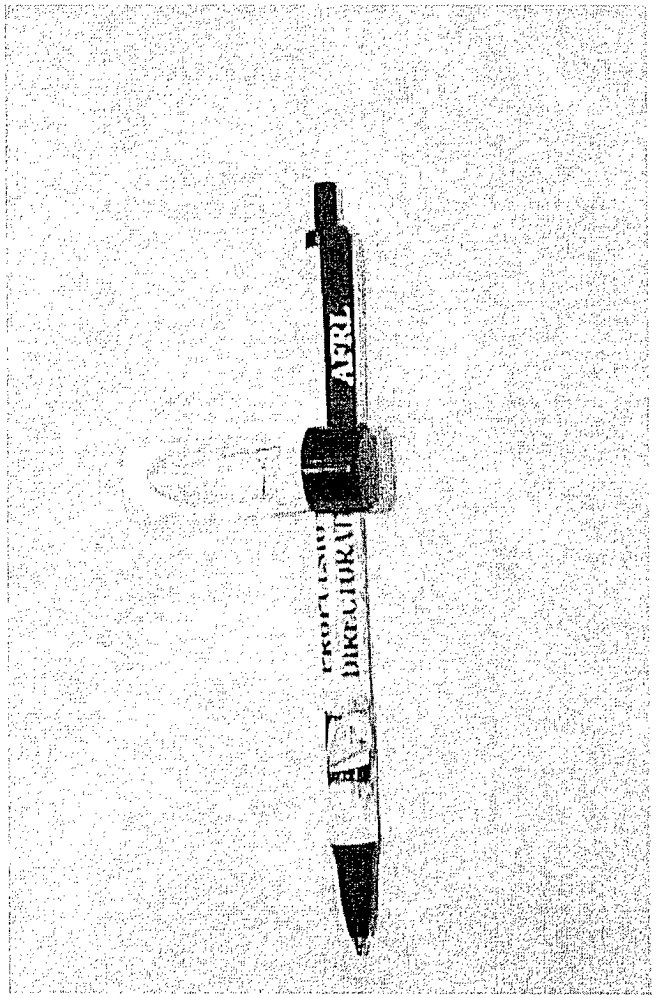
POSS Lubricants/Blends Initial Studies

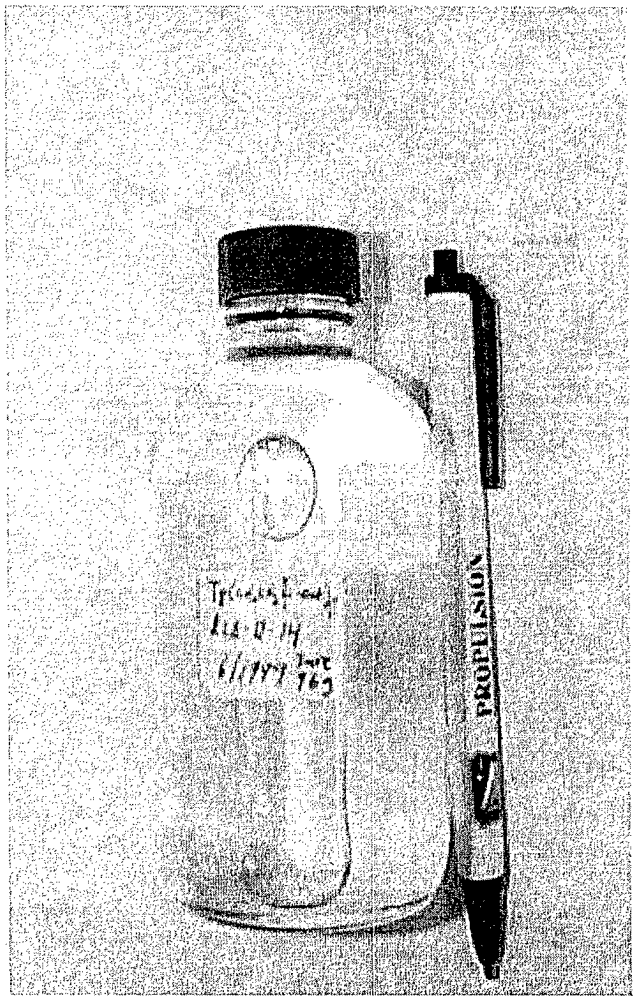


R= $CH_2CH_2SiMe_2Octyl$

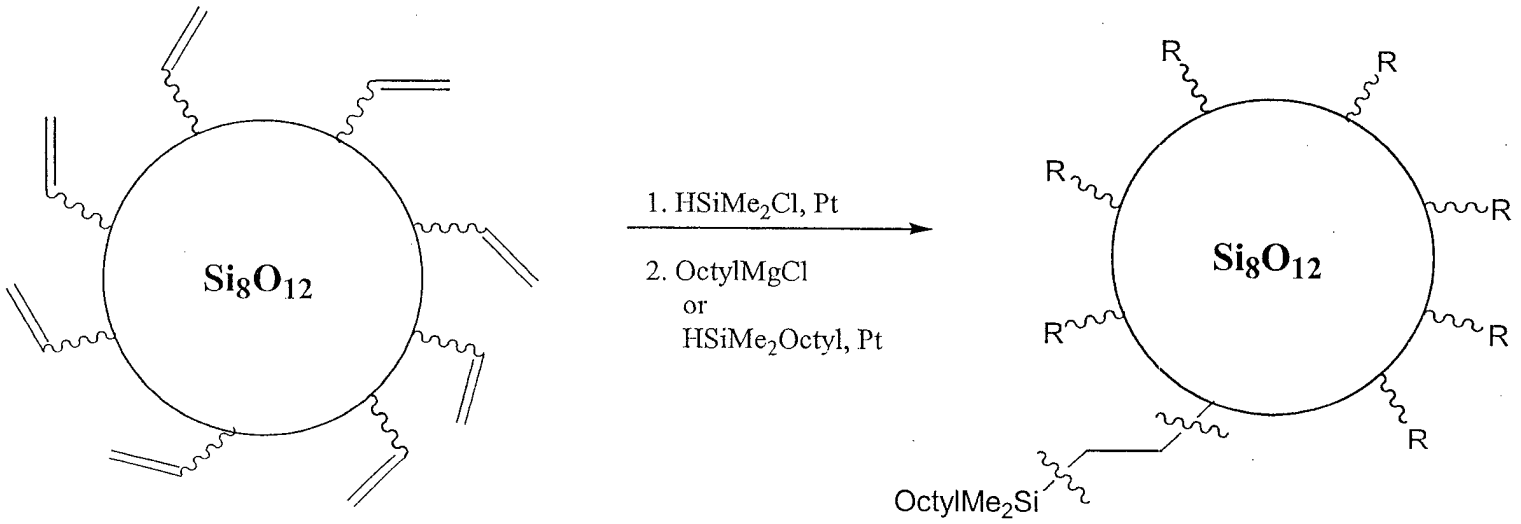
OIL AT RT

POSS Lubricants
$T_8[(CH_2CH_2)SiMe_2Octyl]_8$





POSS Lubricants/Blends
Early work

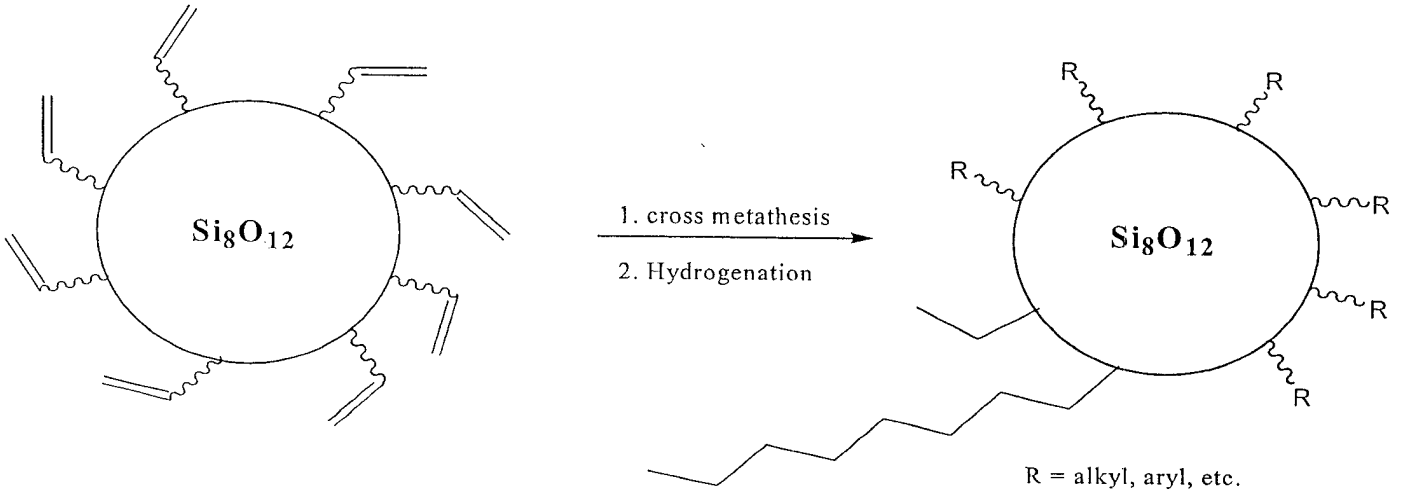


R= $CH_2CH_2SiMe_2Octyl$

OIL AT RT

This class is NOT suitable for High Temp Lubes (Tdec < 200 °C) and decomposes to sand

POSS Lubricants: T8 Class



R = alkyl, aryl, etc.

Octaoctyl:
Tm= 50 C, solid

T8(Octyl)7Ethyl:
Tm= 45C, grease

Stable at 200 °C (TGA)

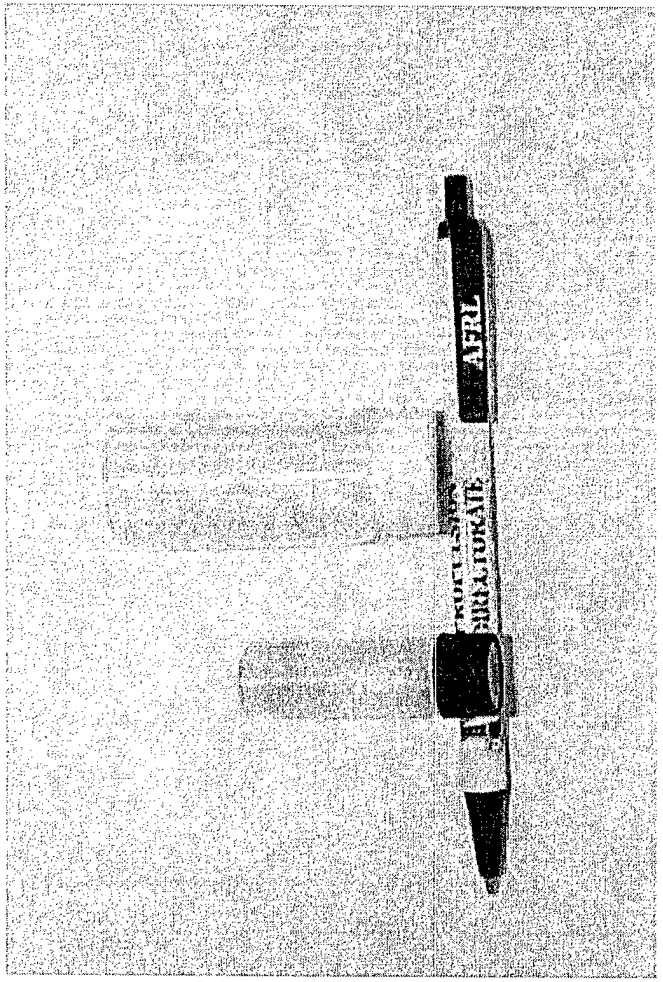
Not an oil, but a possible pathway to oil is shown:

Adjust the organic side groups to disturb any possible order and give a flowable compound

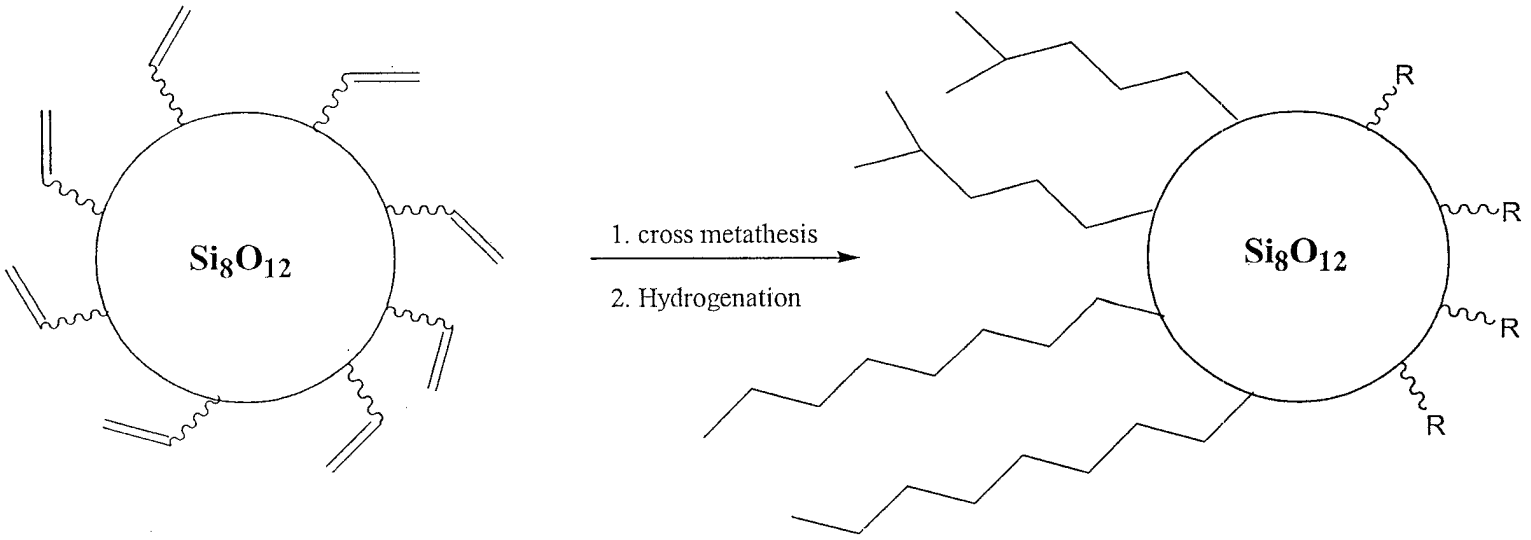
POSS Lubricants: T8 Class

$Octyl_8T_8$ >>>

$Octyl_7EthylT_8$ >>

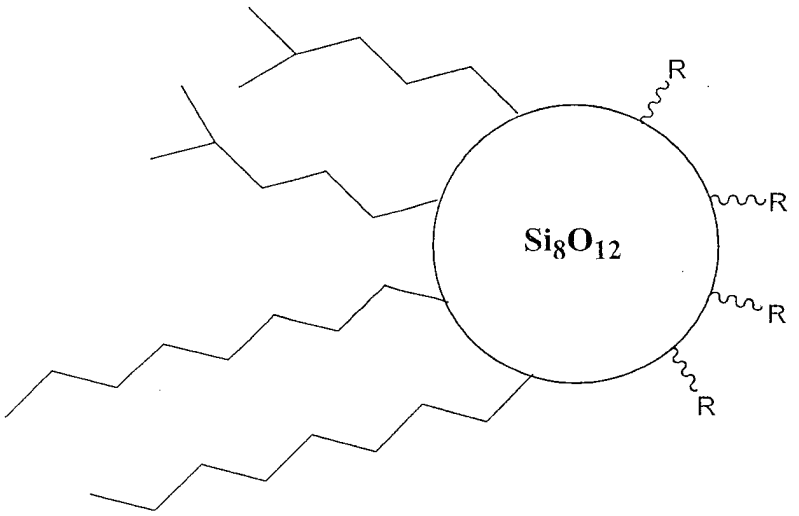


POSS Lubricants
Chain Adjustment Lowers Viscosity

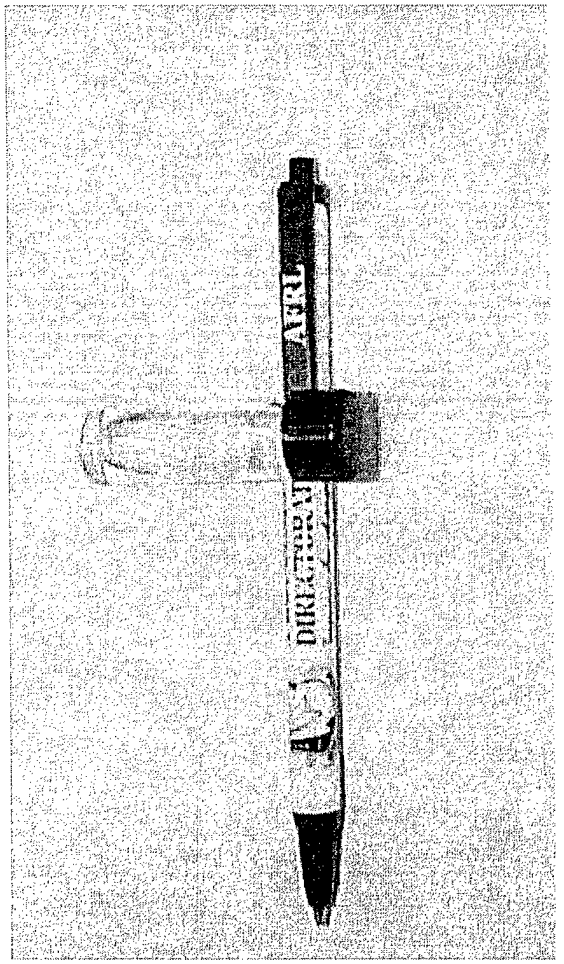


Free flowing oil at room temperature
Viscosity of 1650 centipoise at 0 °C
Freezes at -12 °C
Low volatility

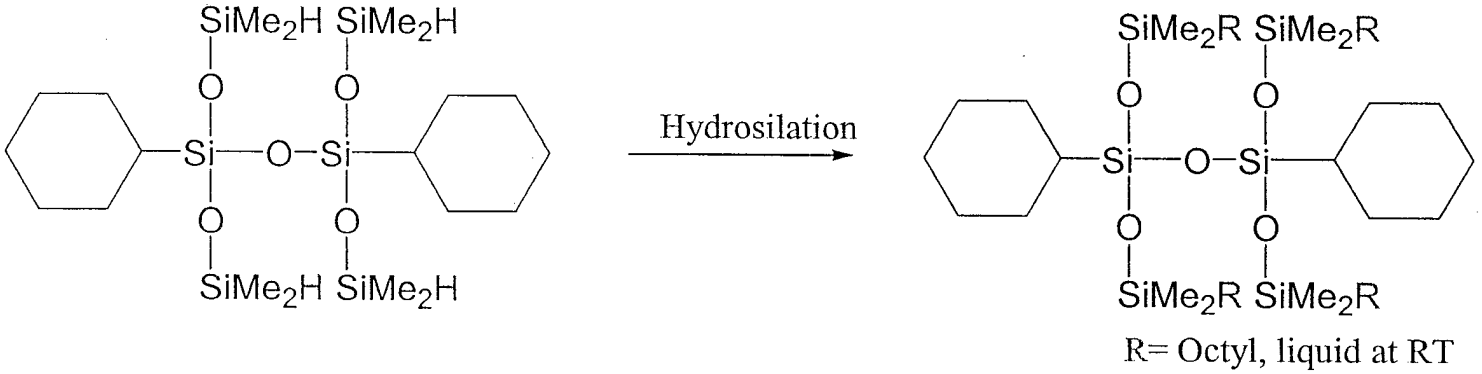
POSS Lubricants
Chain Adjustment Lowers Viscosity



$Octyl_{4.6}T_8$
$4\text{-}Methylpenyl_{3.4}$



POSS Lubricants
CyT_2 Class

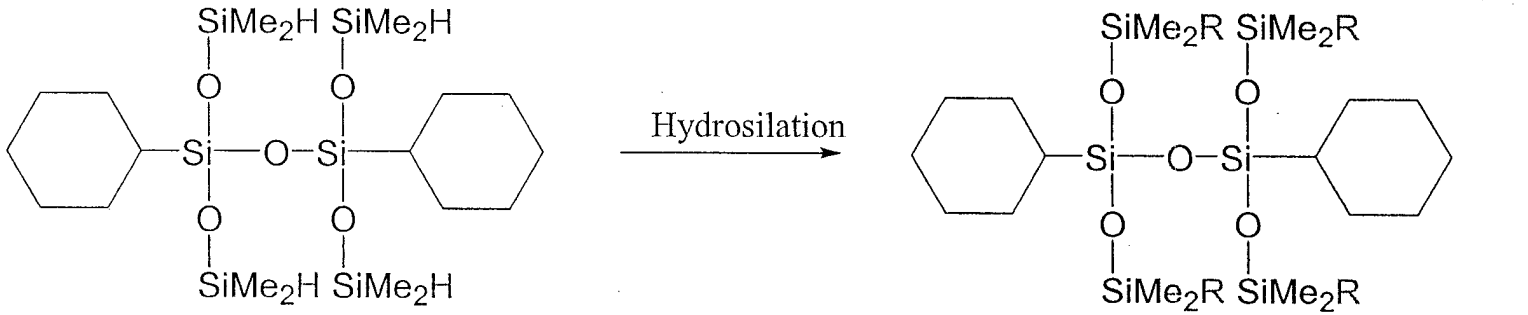


R= Octyl, liquid at RT

Flows even at VERY low temperatures (-60 °C)

Volatility problem at 200 °C > Extend chain length

POSS Lubricants
CyT_2 Class

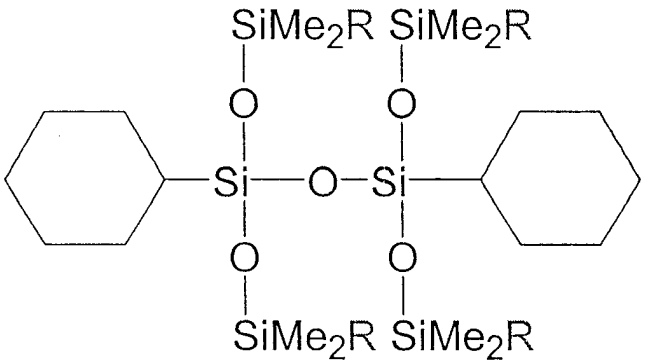


R= Decyl, Dodecyl,
Tetradecyl , all liquids at RT

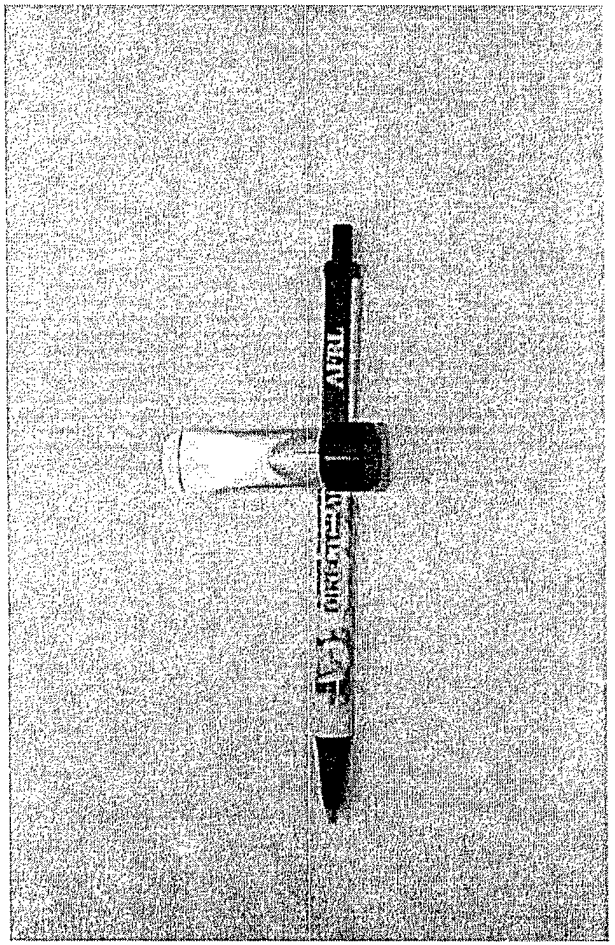
When R=Decyl the viscosity at –40 °C is 4000 cP !!
Stable at 200 °C with A/O present (TGA)

When R=Dodecyl, the freezing point is -12 °C

POSS Lubricants
CyT_2 Class



R= Decyl

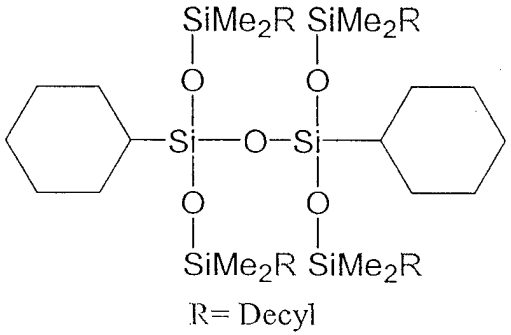


Viscosity of Lubricants

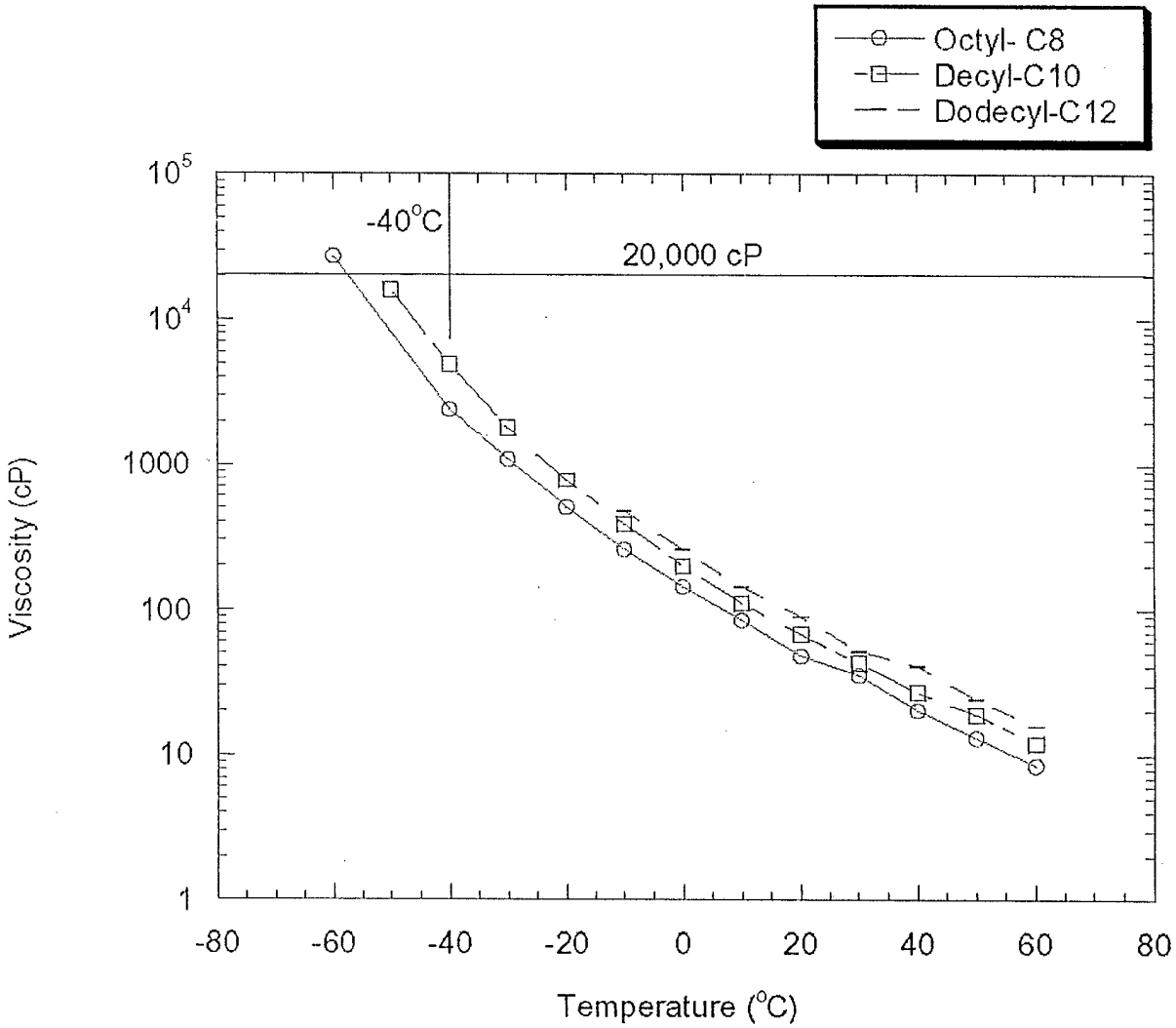
Selected Data for POSS Lubes

Reagent	mp °F	Viscosity cp (T_1°F)	Viscosity cp (T_2°F)	Viscosity cp (T_3°F)
$T_8(octyl)_{4.5}(4\text{-methylpentyl})_{3.5}$	14	1650 (32)	11 (230)	1 (410)
$Cy_2T_2(OSiMe_2Octyl)_4$	< -76	28000(-76)	2600 (-40)	

Viscosity of Lubricants



When R= octyl and decyl, the low temperature pumpable spec (20K cP@ -40 °C) is met!



Decomposition of Lubricants

Selected TGA Data for POSS Lubricants

Reagent	mp °C	iso temp °C	10% wt loss	% lost 9 hrs
Grade 4 Base stock	Liq rt	219.5	30 min	90
$T_8(octyl)_8$	50	218	60 min	27
$T_8(octyl)_7(ethyl)_1$	45	216	225	11
$T_8(octyl)_{4.5}(4\text{-methylpentyl})_{3.5}$	-10	215	391 min	11.6
$Cy_2T_2(OSiMe_2Octyl)_4$	< -40	219	evaporated	100 (evap)
$Cy_2T_2(OSiMe_2Decyl)_4$ w/AO	< -40	205	N/A	1 (4 hours)

Conclusions: POSS Lubricants

-By adjusting organic side groups, POSS oils can be made to flow at low temperature and are stable at higher temperature (Both theT_2s and the larger T_8s)

- Addition of Antioxidant to T2 tetraalkyl derivatives slows down decomposition at 200 °C

Acknowledgments

- Prof. Andre Lee (MSU) for viscosity measurements
- Lubrications Branch (AFRL/PRTM) for helpful discussions and advice
- Hybrid Plastics for materials